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㉓ Compositions for producing polymers of high refractive index and low yellowness.

㉔ The yellowness of polymerizates formed from polymerizable compositions containing bisphenol bis(allylic carbonate)-functional material is reduced by inclusion of one or more cyclohexenic compounds in the polymerizable compositions.

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COMPOSITIONS FOR PRODUCING POLYMERS OF  
HIGH REFRACTIVE INDEX AND LOW YELLOWNESS

Background of the Invention

Aliphatic polyol poly(allyl carbonate) monomer, most notably  
5 diethylene glycol bis(allyl carbonate), has for many years been used  
in producing ophthalmic lenses. Such lenses exhibit low yellowness  
when undyed, substantial hardness, and refractive indices that are  
sufficient for many, if not most, ophthalmic applications. There is a  
need, however, for polymeric lenses of higher refractive indices than  
10 those ordinarily provided by polymers of aliphatic polyol poly(allyl  
carbonate).

This need centers around the desire to reduce the volume of  
material required to produce a lens of given size, minimum thickness,  
and optical correction, which volumetric reduction can be achieved  
15 through use of polymeric materials having higher refractive indices.  
It is known that polymers formed from bisphenol bis(allylic  
carbonate)-functional monomer often have higher refractive indices  
than those formed from aliphatic polyol poly(allyl carbonate) monomer,  
but the former polymers usually exhibit excessive yellowness to be  
20 widely acceptable for ophthalmic purposes.

The present invention is directed to polymerizates having  
high refractive index and low yellowness, and to polymerizable,  
homogeneous compositions which may be free radically polymerized to  
produce such polymerizates.

25 It has been discovered that the yellowness of polymerizates  
formed from polymerizable compositions containing bisphenol  
bis(allylic carbonate)-functional material may be reduced if one or  
more cyclohexenic compounds are included in the polymerizable  
compositions.

Accordingly, one embodiment of the invention is polymerizable, homogeneous composition comprising bisphenol bis(allylic carbonate)-functional material comprising (i) bisphenol bis(allylic carbonate)-functional monomer, (ii) prepolymer of such monomer, or (iii) a mixture thereof, characterized in that the composition also comprises a yellowness reducing amount of a cyclohexenic material which is a cyclohexenic compound or a mixture of such cyclohexenic compounds, and optionally (b) one or more other materials.

10 As used herein and in the claims, "a yellowness reducing amount of cyclohexenic material" means an amount of cyclohexenic material in the polymerizable composition which will cause the yellowness of a polymerizate formed from the polymerizable composition to be lower than that of a polymerizate formed under similar 15 conditions from a similar polymerizable composition not containing any cyclohexenic material.

Another embodiment of the invention is polymerizate characterized in that the polymerizate is produced by free-radically polymerizing the polymerizable, homogeneous composition of the first 20 embodiment, and the polymerizate has a 15-second Barcol hardness of at least zero, a yellowness index at a sample thickness of about 3.3 millimeters of about 4 or lower, and a refractive index at 20°C and a wavelength of 589.3 nanometers of at least about 1.52.

In most cases the polymerizable, homogeneous compositions of 25 the invention are pourable. The term "pourable" as used herein and in the accompanying claims means the viscosity of the composition is sufficiently low that it can be poured into molds commonly used in casting ophthalmic lenses and lens blanks. The temperature of reference is usually ambient temperature, but in some cases slightly 30 elevated temperatures are employed to reduce the viscosity and facilitate pouring. In those instances where the composition contains free-radical initiator, the temperature should ordinarily be below that at which polymerization is initiated. Ordinarily the viscosity of the material is at least as low as about 6000 centipoises at 25°C. 35 In many cases the viscosity is at least as low as about 2000 centipoises at 25°C. Often the viscosity is at least as low as about

500 centipoises at 25°C. It is preferred that the viscosity be at least as low as about 100 centipoises at 25°C.

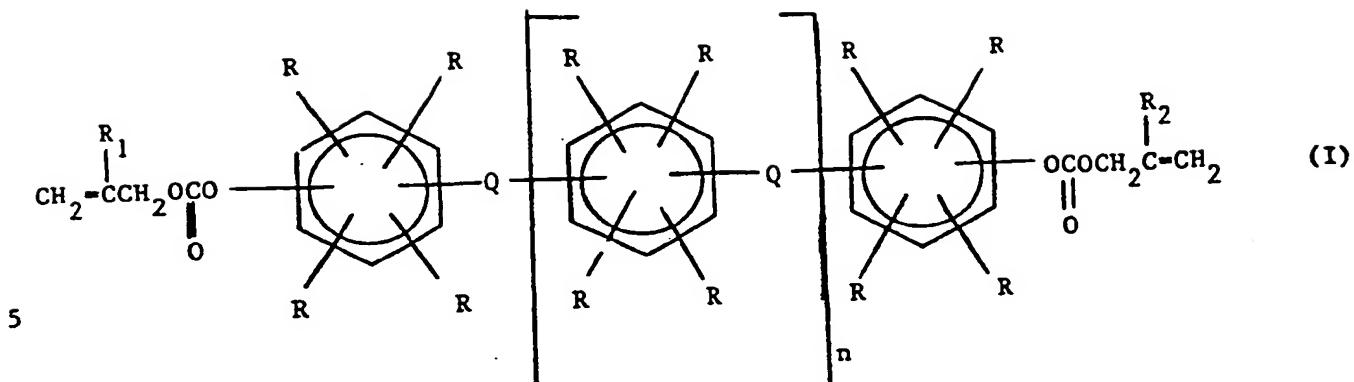
The bisphenol bis(allylic carbonate)-functional monomer can be prepared by procedures well known in the art. In one method, the 5 appropriate allyl alcohol is reacted with phosgene to form the corresponding allyl chloroformate which is then reacted with the desired bisphenol. In another method, the bisphenol is reacted with phosgene to form bischloroformate of the bisphenol which is then reacted with the appropriate allyl alcohol. In a third method, the 10 bisphenol, the appropriate allyl alcohol, and phosgene are mixed together and reacted. In all of these reactions the proportions of reactants are approximately stoichiometric, except that phosgene may be used in substantial excess if desired. The temperatures of the chloroformate-forming reactions are preferably below about 100°C in 15 order to minimize the formation of undesirable by-products.

Ordinarily the temperature of the chloroformate-forming reaction is in the range of from about 0°C to about 20°C. The carbonate-forming reaction is usually conducted at about the same temperatures, although higher temperatures may be employed. Suitable acid acceptors, e.g., 20 pyridine, a tertiary amine, an alkali metal hydroxide, or an alkaline earth metal hydroxide may be employed when desired. See, for example, United States Patent Nos. 2,455,652; 2,455,653; and 2,587,437.

Ordinarily the bisphenol bis(allylic carbonate)-functional monomer comprises a bisphenol bis(allylic carbonate)-functional 25 monomeric compound containing at least two phenylene groups separated by oxy, sulfonyl, thio, alkanediyl, or alkylidene; or a mixture of such compounds.

Preferably, the bisphenol bis(allylic carbonate)-functional material comprises a bis(allylic carbonate)-functional monomeric 30 compound containing at least two phenylene groups separated by oxy, sulfonyl, thio, alkanediyl, or alkylidene; or a mixture of such compounds.

A subclass of monomeric compound which is of particular usefulness is represented by the formula



wherein (a) each R of the monomeric compound is independently hydrogen, halo, alkyl, or alkoxy, (b) each Q of the monomeric compound is independently oxy, sulfonyl, thio, alkanediyl, or alkylidene, (c)  $R_1$  and  $R_2$  are each independently hydrogen or methyl, and (d) the value of  $n$  is an integer in the range of from 0 to about 3.

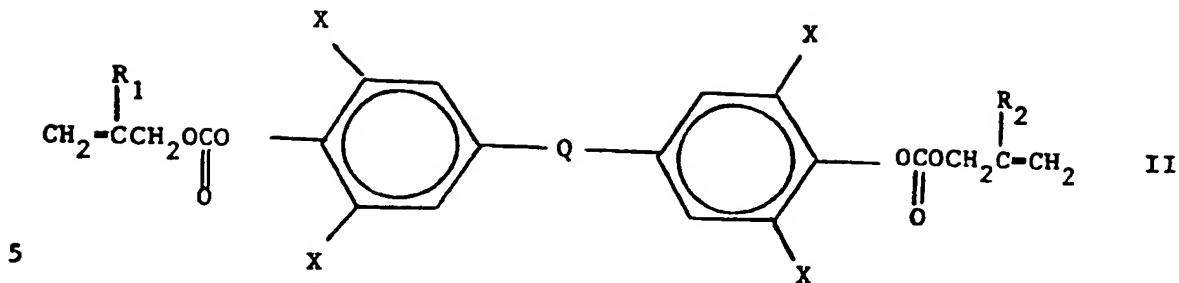
In most cases the various groups represented by R are the same or some are different from others. When an R is halogen, it is most commonly chloro or bromo. When an R is alkyl, it usually contains from 1 to 15 about 4 carbon atoms; methyl is preferred. When an R is alkoxy, it usually contains from 1 to about 4 carbon atoms; methoxy is preferred. It is especially preferred that each R be hydrogen.

Similarly, when  $n$  is a positive integer, the various groups represented by Q may be the same or they may differ. When a Q is alkanediyl, it ordinarily contains from 2 to about 4 carbon atoms; ethanediyl is preferred. When a Q is alkylidene, it usually contains from 1 to about 5 carbon atoms; methylethylidene, viz., isopropylidene, is preferred.

$R_1$  and  $R_2$  may be different, but ordinarily they are the same. It is preferred that  $R_1$  and  $R_2$  are both hydrogen.

For any particular compound,  $n$  is an integer in the range of from 0 to about 3. In most cases  $n$  is either 0 or 1. Preferably, the value of  $n$  is zero. While the value of  $n$  is an integer for an individual compound, it may be a whole or fractional number in the range of from 0 to about 3 when Formula I is used to represent mixtures of compounds falling therein.

The preferred monomeric compounds are those represented by the formula

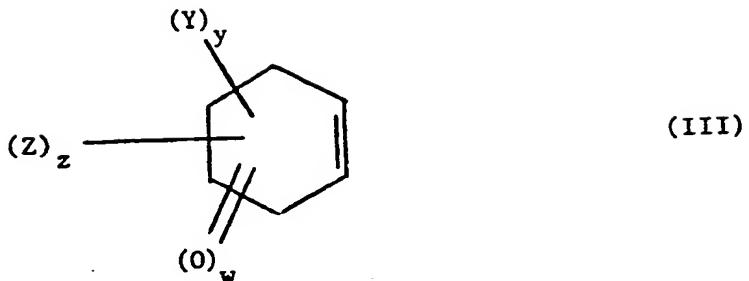


5 wherein (a) each X of the monomeric compound is independently hydrogen, chloro, or bromo, (b) Q is oxy, sulfonyl, thio, alkanediyl, or alkylidene, and (c) R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or methyl. The above discussion in respect of Q, R<sub>1</sub>, and R<sub>2</sub> is  
10 applicable to Formula II. Some the the groups represented by X may be different from the others, but preferably all of the groups represented by X are the same.

Examples of monomeric compounds that may be used in the invention include the bis(allyl carbonate) and the bis(methallyl carbonate) of bisphenols such as 4,4'-(1-methylethylidene)bis(phenol), 15 4,4'-(1-methylethylidene)bis(2,6-dibromophenol), 4,4'-(1-methylethylidene)bis(2,6-dichlorophenol), 4,4'-(1-methylpropylidene)bis(phenol), 4,4'-(methylene)bis(phenol), 2,2'-(methylene)bis(phenol), 4,4'-(sulfonyl)bis(phenol), 20 4,4'-(thio)bis(phenol), 4,4'-(oxy)bis(phenol), 4,4'-(oxy)bis(chlorophenol), 4,4'-(oxy)bis(dimethylphenol), 4,4'-[1,4-phenylenebis(1-methylethylidene)]bis(phenol), 4,4'-[1,3-phenylenebis(1-methylethylidene)]bis(phenol), 3,3'-[1,4-phenylenebis(oxy)]bis(phenol), 25 4,4'-[1,4-phenylenebis(oxy)]bis(phenol), 4,4'-[{2,5-bis(1,1-dimethylethyl)-1,4-phenylene}bis(oxy)]-bis[2,6-bis(1,1-dimethylethyl)phenol], and 4,4'-[1,4-phenylenebis(sulfonyl)]-bis(phenol).

The preferred monomeric compound is the bis(allyl carbonate) 30 of 4,4'-(1-methylethylidene)bis(phenol), which is commonly known as bisphenol A bis(allyl carbonate).

A wide variety of cyclohexenic compounds may be used in the practice of this invention. Ordinarily the cyclohexenic material comprises at least one cyclohexenic compound represented by the formula



in which (a) each Y is independently alkyl containing from 1 to about 4 carbon atoms, (b) Z is hydroxyl, 2-oxoethyl, hydroxyalkyl containing from 1 to about 3 carbon atoms, alkoxy carbonyl containing from 2 to 10 about 5 carbon atoms, or  $R_3C(O)OR_4$  - in which  $R_3$  is alkyl containing from 1 to about 4 carbon atoms and  $R_4$  is alkanediyl containing from 2 to about 4 carbon atoms or alkylidene containing from 1 to about 5 carbon atoms, (c)  $y$  is an integer in the range of from 0 to about 3, (d)  $z$  is 0 or 1, (e)  $w$  is 0 or 1, and (f) the sum 15 of  $z$  and  $w$  is 0 or 1.

Methyl is the preferred alkyl group used for Y. The groups represented by Y may be the same or they may differ.

When Z is hydroxyalkyl, it is usually hydroxymethyl, 2-hydroxyethyl, or 1-hydroxy-1-methylethyl. When Z is alkoxy carbonyl, 20 it usually contains 2 or 3 carbon atoms. Methoxycarbonyl is preferred.  $R_3$  is most often methyl, ethyl or propyl. When  $R_4$  is alkanediyl, it may be straight or branched; ethanediyl is preferred. When  $R_4$  is alkylidene it is usually methylene or 1-methylethylidene. Preferably  $y$  is 0 or 1. Similarly it is 25 preferred that  $z$  be 0 or 1. It is also preferred that  $w$  be zero.

Examples of cyclohexenic compounds that may be used in the invention include cyclohexene,  $\alpha$ -terpineol, terpinen-4-ol,  $\alpha$ -terpinyl acetate,  $\alpha$ -terpinyl propionate,  $\alpha$ -terpinyl butyrate, 30 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, methyl 1-cyclohexene-1-carboxylate, 3-methyl-2-cyclohexen-1-ol, 3-methyl-2-cyclohexen-1-one, 4-isopropyl-2-cyclohexen-1-one, 3,5-dimethyl-2-cyclohexen-1-one, 4,4-dimethyl-2-cyclohexen-1-one, isophorone, 2,6,6-trimethyl-1-cyclohexene-1-acetaldehyde, and 3,5,5-trimethyl-2-cyclohexen-1-ol. The pre-

ferred cyclohexenic compounds are cyclohexene,  $\alpha$ -terpinyl acetate,  $\alpha$ -terpinyl propionate, and  $\alpha$ -terpinyl butyrate. The especially preferred cyclohexenic material is cyclohexene,  $\alpha$ -terpinyl acetate, or a mixture thereof.

5 The bisphenol poly(allylic carbonate)-functional prepolymer which is useful in the practice of the present invention is prepared by partially polymerizing bisphenol bis(allylic carbonate)-functional monomer to utilize a fraction of the allylic groups without incurring significant gellation. The preferred bisphenol poly(allylic 10 carbonate)-functional prepolymers are those prepared in accordance with the procedures described in detail in European Patent Office Publication No. 0 114 782.

In accordance with a method of European Patent Office Publication No. 0 114 782, bisphenol bis(allylic carbonate)-functional 15 monomer is dissolved in a solvent in which the polymer produced from such monomer is also soluble. Preferably, the initiator used to conduct the polymerization is also soluble in the solvent. The resulting liquid solution comprising bisphenol bis(allylic carbonate)-functional monomer, solvent, and preferably initiator is 20 then partially polymerized, e.g., by heating the liquid solution to polymerization temperatures. The polymerization reaction is allowed to continue until more than 12 percent allylic utilization is attained, i.e., until more than 12 percent of the unsaturated carbon - carbon linkages in the monomer are consumed. The degree of allylic 25 utilization can be controlled by regulating the amount of initiator added to the liquid solution, the temperature at which the partial polymerization is performed, and the ratio of solvent to bisphenol bis(allylic carbonate)-functional monomer. Generally, the greater the amount of initiator used, the higher is the allylic utilization. The 30 higher the temperature of polymerization, the lower is the degree of allylic utilization. At constant temperature and employing a given amount of initiator, the higher the ratio of solvent to monomer, the lower is the degree of allylic utilization. Ordinarily however, if at constant temperature the ratio of solvent to monomer is increased and 35 the amount of initiator employed is also sufficiently increased, the reaction can be driven to a higher degree of allylic utilization

without the formation of gel than in a system containing less solvent.

In a preferred embodiment of European Patent Office Application No. 0 114 782, from about 0.1 to about 1.5 weight percent 5 of initiator, basis the amount of monomer, from about 0.5 to 5 milliliters of solvent per gram of monomer, and polymerization temperatures of from 28°C to about 100°C are used. The degree of allylic utilization can be monitored by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. The solvent in the resulting 10 composition can be removed by known techniques, e.g., by evaporation or distillation, leaving a viscous liquid comprising a solution of bisphenol poly(allylic carbonate)-functional prepolymer in bisphenol bis(allylic carbonate)-functional monomer. This solution is typically 15 a syrupy liquid having a kinematic viscosity (measured with a capillary viscometer) of from at least about 100 centistokes to about 100,000 centistokes, typically from about 1000 to 40,000 centistokes, more typically from about 500 to 2,000 centistokes, measured at 25°C., and a bulk density at 25°C. of from about 1.1 to about 1.23 grams per cubic centimeter. The solution is further characterized by having 20 more than 12 percent allylic utilization, preferably from at least 15 to 50 percent allylic utilization, and, in a particularly preferred exemplification, from about 20 to 50 percent allylic utilization, as determined by infrared spectroscopy (IR) or nuclear magnetic resonance 25 spectroscopy (NMR).

Organic solvents useful in carrying out the solution polymerization are those which are non-reactive chemically with the monomer and resulting polymer, have a boiling temperature substantially below the monomer, i.e., a higher vapor pressure, so as to be easily separated from the monomer by distillation, and which 30 serve as a solvent for the bisphenol bis(allylic carbonate)-functional monomer and the resulting bisphenol poly(allylic carbonate)-functional prepolymer (and preferably also the initiator). Useful solvents include the halogenated, e.g., chlorinated, C<sub>1</sub>-C<sub>2</sub> hydrocarbon solvents, i.e., methyl chloride, methylene chloride, ethyl chloride, 35 ethylene dichloride, 1,1,2-trichloro-1,2,2-trifluoroethane, and mixtures thereof. Methylene chloride is preferred because of its high

vapor pressure, low boiling point, ease of separation, and relatively low toxicity.

The amount of solvent used in the partial polymerization process should be sufficient to solubilize all of the monomer and to maintain all of the resulting prepolymer in solution. This is generally from about 0.5 to 5 milliliters of solvent per gram of monomer. Greater amounts of solvent can be used without deleterious effect. Lesser amounts of solvent often result in the formation of an insoluble, infusible, intractable gel when allylic utilizations above about 17 percent are employed.

The concentration of initiator useful for the partial polymerization should be sufficient to result in the desired degree of allylic utilization at the conditions used, and generally can vary from 0.1 to about 1.5 weight percent initiator, basis weight of monomer. Greater amounts of initiator may result in either residual initiator in the product or formation of an infusible, insoluble, intractable gel. The initiators useful in carrying out the solution polymerization of the bisphenol bis(allylic carbonate)-functional monomer are free radical initiators, e.g., organic peroxides and azo catalysts, and are well known in the art. The preferred free radical initiators are organic peroxy compounds, such as peroxyesters, diacyl peroxides peroxydicarbonates and mixtures of such peroxy compounds.

Examples of peroxy compounds include: peroxydicarbonate esters such as di-n-propyl peroxydicarbonate, diisopropyl 25 peroxydicarbonate, di-n-butyl peroxydicarbonate, di-sec-butyl peroxydicarbonate, diisobutyl peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, diacetyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, and isopropyl sec-butyl peroxydicarbonate; diacetyl peroxides such as 30 diacetyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, and diisobutyryl peroxide; and peroxyesters such as tertiary-butyl perpivalate, tertiary-butyl peroctoate and tertiary-butyl perneodecanoate.

Only one peroxy compound or a mixture of peroxy compounds 35 may be used as desired.

The solution polymerization is generally carried out at temperatures of from about 28°C. to about 100°C., for from about 1 to about 24 hours. The time and temperature depend on the initiator and the concentration thereof, and the solvent:monomer ratio used.

5 The amount of bisphenol bis(allylic carbonate)-functional material present in the polymerizable, homogeneous composition is susceptible to wide variation. Ordinarily, the bisphenol bis(allylic carbonate)-functional material is present in the polymerizable, homogeneous composition in an amount in the range of from about 40 to 10 about 99.9 percent by weight. Often it is present in an amount in the range of from about 50 to about 99.5 percent by weight. An amount in the range of from about 85 to about 99 percent by weight is preferred.

15 Similarly the amount of cyclohexenic material present in the polymerizable, homogeneous composition may be widely varied. Generally the cyclohexenic material is present in the polymerizable, homogeneous composition in an amount in the range of from about 0.1 to about 5 percent by weight. In many cases it is present in an amount in the range of from about 0.5 to about 4 percent by weight. An 20 amount in the range of from about 1 to about 3 percent by weight is preferred.

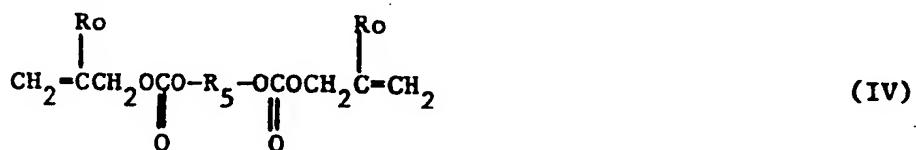
There are many materials which may optionally be present in the polymerizable, homogeneous composition.

25 Non-aromatic bis(allylic carbonate)-functional monomer is a material which can optionally be present in the polymerizable homogeneous compositions of the invention. Such monomer comprises one or more non-aromatic bis(allylic carbonate)-functional monomeric compounds which are bis(allylic carbonates) of linear or branched aliphatic glycols, cycloaliphatic glycols, or glycols containing at 30 least one divalent aliphatic portion and at least one divalent cycloaliphatic portion. These monomers can be prepared by procedures well known in the art, for example, those described in United States Patent Nos. 2,370,567 and 2,403,113. In the latter patent, the monomers are prepared by treating the non-aromatic glycol with 35 phosgene at temperatures between 0°C and 20°C to form the corresponding bischloroformate. The bischloroformate is then reacted

with an unsaturated alcohol in the presence of a suitable acid acceptor, as for example, pyridine, a tertiary amine, or an alkali or alkaline earth metal hydroxide. Alternatively, the unsaturated alcohol can be reacted with phosgene and the resulting chloroformate 5 reacted with the non-aromatic glycol in the presence of an alkaline reagent, as described in United States Patent No. 2,370,567.

The non-aromatic bis(allylic carbonate)-functional monomeric compounds can be represented by the formula

10



in which  $\text{R}_5$  is the divalent radical derived from the non-aromatic glycol and each  $\text{Ro}$  is independently hydrogen, halo, or an alkyl group 15 containing from 1 to about 4 carbon atoms. The alkyl group is usually methyl or ethyl. Most commonly both groups represented by  $\text{Ro}$  are hydrogen or methyl; hydrogen is preferred.

The aliphatic glycol from which the non-aromatic bis(allylic carbonate)-functional monomeric compound may be derived, can be linear 20 or branched and contain from 2 to about 10 carbon atoms. Commonly, the aliphatic glycol is an alkylene glycol having from 2 to 4 carbon atoms or a poly( $\text{C}_2\text{-C}_4$ ) alkylene glycol. Examples of such compounds include ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 25 1,8-octanediol, 2-ethylhexyl-1,6-diol, 1,10-decanediol, diethylene glycol, triethylene glycol, tetraethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ , dipropylene glycol, tripropylene glycol, and tetrapropylene glycol. Other examples include alkylene carbonate and alkylene ether carbonate diols such as 30  $\text{HOCH}_2\text{CH}_2\text{O-CO-OCH}_2\text{CH}_2\text{OH}$  and  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O-CO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ .

The cycloaliphatic glycols from which the non-aromatic bis(allylic carbonate)-functional monomeric compound may be derived, usually contain from about 5 to about 8 carbon atoms. Ordinarily, the cycloaliphatic glycol contains from about 6 to about 8 carbon atoms. Examples

include 1,3-cyclopentanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol and 1,5-cyclooctanediol.

Examples of glycols containing at least one divalent aliphatic portion and at least one cycloaliphatic portion which may be used include 4,4'-methylenebis(cyclohexanol), 4,4'-(1-methylethylidene)bis(cyclohexanol), 2,2'-(1,4-cyclohexanediyl)bisethanol, and 1,4-cyclohexane dimethanol.

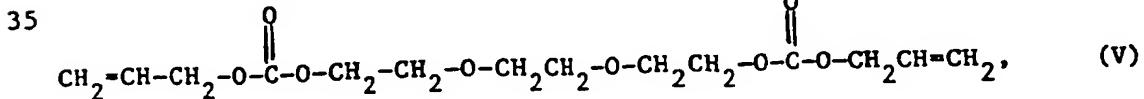
The non-aromatic glycol from which the non-aromatic bis(allylic carbonate)-functional monomeric compound may be derived may also be aliphatic diol-functional chain extended compounds.

Examples of such compounds based on alkylene oxide extension include ethylene oxide extended trimethylolpropane, propylene oxide extended trimethylolpropane, ethylene oxide extended glycerol, and propylene oxide extended glycerol.

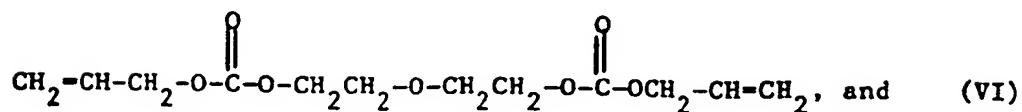
Preferably, the non-aromatic bis(allylic carbonate)-functional monomeric compound is aliphatic bis(allylic carbonate)-functional monomer-ic compound. Most commonly, R<sub>5</sub> is -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>-, or -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>-.

Specific examples of aliphatic bis(allylic carbonate)-functional monomeric compounds useful in the practice of the invention include ethylene glycol bis(2-chloroallyl carbonate), ethylene glycol bis(allyl carbonate), 1,4-butanediol bis(allyl carbonate), 1,5-pentane-25 diol bis(allyl carbonate), 1,6-hexanediol bis(allyl carbonate), diethylene glycol bis(2-methallyl carbonate), diethylene glycol bis(allyl carbonate), triethylene glycol bis(allyl carbonate), propylene glycol bis(2-ethylallyl carbonate), 1,3-propanediol bis(allyl carbonate), 1,3-butane-30 diol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl carbonate), and pentamethylene glycol bis(allyl carbonate).

Industrially important aliphatic bis(allyl carbonate)-functional monomeric compounds which can be utilized in the invention herein contemplated are:

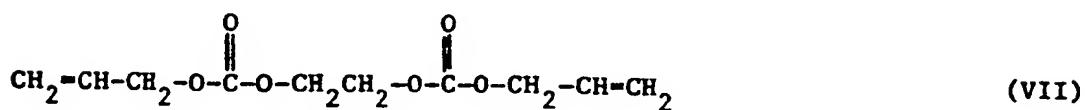


Triethylene Glycol bis(Allyl Carbonate)



Diethylene Glycol bis(Allyl Carbonate)

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Ethylene Glycol bis(Allyl Carbonate)

Diethylene glycol bis(allyl carbonate) is preferred. Monomer containing 10 this compound is commercially available from PPG Industries, Inc. and is sold under the trademark CR-39 Allyl Diglycol Carbonate.

The amount of non-aromatic bis(allylic carbonate)-functional monomer present in the polymerizable, homogeneous composition may be widely varied. When it is used, the weight ratio of the non-aromatic bis-15 (allylic carbonate)-functional monomer to all ethylenically unsaturated material present in the composition is ordinarily in the range of from about 0.1:100 to about 20:100. Often the weight ratio is in the range of from about 1:100 to about 15:100. A weight ratio in the range of from about 2:100 to about 10:100 is preferred.

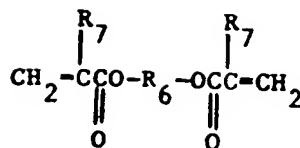
20 Another material which may optionally be present is non-aromatic poly(allylic carbonate)-functional prepolymer. This material is prepared by partially polymerizing non-aromatic poly(allylic carbonate)-functional monomer to utilize a fraction of the allylic groups without incurring significant gellation. The preferred non-aromatic poly(allylic 25 carbonate)-functional prepolymers are those prepared in accordance with the procedures described in detail in European Patent Office Application No. 0 114 782. The preparation is analogous to the preparation of the bisphenol poly(allylic carbonate)-functional prepolymer, except that non-aromatic poly(allylic carbonate)-functional monomer is used rather 30 than bisphenol bis(allylic carbonate)-functional monomer. Following partial polymerization, the solvent in the composition can be removed by known techniques, e.g., by evaporation or distillation, leaving a viscous liquid comprising a solution of non-aromatic poly(allylic carbonate)-functional prepolymer in non-aromatic bis(allyl carbonate)-func-

tional monomer. The solution is typically a pourable, syrupy liquid having a kinematic viscosity (measured with a capillary viscometer) of from at least about 100 centistokes to about 100,000 centistokes, typically from about 1000 to 40,000 centistokes, more typically from 5 about 500 to 2,000 centistokes, measured at 25°C., and a bulk density at 25°C. of from about 1.17 to about 1.23 grams per cubic centimeter. The solution is further characterized by having more than 12 percent allylic utilization, preferably from at least 15 to 50 percent allylic utilization, and, in a particularly preferred exemplification, from 10 about 20 to 50 percent allylic utilization, as determined by IR or NMR analysis. IR analysis is preferred.

According to one exemplification, a liquid mixture comprising 100 grams of diethylene glycol bis(allyl carbonate) monomer, 300 milliliters of methylene chloride and 1.1 milliliters of 15 diisopropyl peroxydicarbonate was prepared. The liquid mixture was placed in a bottle and the bottle was purged with argon for 3 minutes. The bottle and its contents were held at 70°C for 18 hours and then cooled to 25°C. The liquid reaction mixture was placed in a one-liter round bottom flask and vacuum stripped at 50°C for 2 hours. 20 Then the temperature was raised to 60°C for 1 hour and the pressure lowered until an absolute pressure of 267 pascals was obtained. The residue remaining after vacuum stripping was a solution of aliphatic poly(allyl carbonate)-functional prepolymer in diethylene glycol bis(allyl carbonate) monomer and had a viscosity of 1900 centipoises 25 and an allylic utilization of 34 percent.

The amount of non-aromatic poly(allyl carbonate)-functional prepolymer present in the polymerizable, homogeneous composition may be widely varied. When it is used, the weight ratio of the non-aromatic poly(allyl carbonate)-functional polymer to all 30 ethylenically unsaturated material present in the composition is ordinarily in the range of from about 0.1:100 to about 20:100. Often the weight ratio is in the range of from about 1:100 to about 15:100. A weight ratio in the range of from about 2:100 to about 10:100 is preferred.

35 Another material that may optionally be present is diester represented by the formula

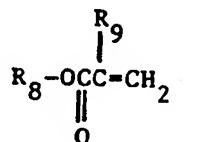


(VIII)

where  $\text{R}_6$  is a divalent organo group which may be aromatic, non-aromatic, or partially aromatic and partially non-aromatic, and where each  $\text{R}_7$  is independently hydrogen, halo, or an alkyl group containing from 1 to about 4 carbon atoms. Usually, both groups represented by  $\text{R}_7$  are either hydrogen or both are methyl. These diesters are esterification products of dihydroxy-functional materials 10 with one or more acrylic acids. They are known compounds and may be prepared by well known procedures.

The amount of the diester present in the polymerizable, homogeneous composition may also be widely varied. When it is used, the weight ratio of the diester to all ethylenically unsaturated material 15 present in the composition is generally in the range of from about 0.1:100 to about 20:100. Typically the weight ratio is in the range of from about 1:100 to about 15:100. A weight ratio in the range of from about 2:100 to about 10:100 is preferred.

Yet another optional material which may be present is 20 monofunctional acrylate represented by the formula



(IX)

where  $\text{R}_8$  is a monovalent organo group and  $\text{R}_9$  is hydrogen, halo, or 25 an alkyl group containing from 1 to about 4 carbon atoms.

The monofunctional acrylates represented by Formula IX are themselves well known compounds. The monovalent organo group,  $\text{R}_8$ , may be aliphatic, cycloaliphatic, aromatic, or a combination of two or more of these properties. Most often  $\text{R}_8$  is alkyl containing from 1 30 to about 4 carbon atoms, cycloalkyl containing from 5 to about 8 carbon atoms, phenyl, or benzyl. It is preferred that  $\text{R}_8$  be methyl, ethyl, isobutyl cycloalkyl, phenyl, or benzyl.  $\text{R}_9$  is usually hydrogen or methyl. Examples of monofunctional acrylates include: methyl acrylate, methyl methacrylate, ethyl methacrylate, butyl

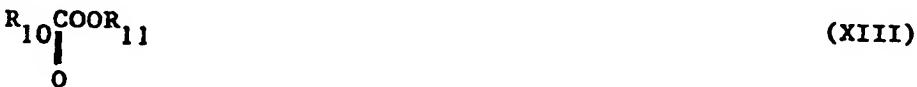
methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, phenyl methacrylate, and benzyl methacrylate. The methacrylic acid esters, as for example isobutyl methacrylate, are preferred.

The amount of monofunctional acrylate present in the polymerizable, homogeneous composition may be varied considerably. When the monofunctional acrylate is used, the weight ratio of the monofunctional acrylate to all ethylenically unsaturated material present in the composition is ordinarily in the range of from about 0.1:100 to about 25:100. Often the weight ratio is in the range of 10 from about 1:100 to about 15:100. A weight ratio in the range of from about 2:100 to about 10:100 is preferred. A weight ratio in the range of from about 3.5:100 to about 5.5:100 is especially preferred.

One or more ethylenically unsaturated monomers not heretofore discussed may optionally be present in the pourable, polymerizable composition of the invention. Illustrative of such monomers are alkyl esters of ethylenically unsaturated dicarboxylic acids, cycloalkyl esters of ethylenically unsaturated dicarboxylic acids, allyl esters of saturated or ethylenically unsaturated dicarboxylic acids, vinyl esters of saturated monocarboxylic acids, 20 vinyl benzoate, styrene, substituted styrene, divinylbenzene, diallylic esters of any of the phthalic acids, tris and higher functional acrylates, tris and higher functional allylic compounds which include tris and higher functional allylic carbonate compounds. It is preferred that the vinyl esters of saturated monocarboxylic acids contain from 4 to about 6 carbon atoms. Vinyl acetate is especially preferred. When used, the weight ratio of these materials to all ethylenically unsaturated material present in the composition is usually in the range of from about 0.1:100 to about 15:100. A weight ratio in the range of from about 0.1:100 to about 10:100 is preferred. When used, the weight ratio of vinyl ester of saturated 30 monocarboxylic acid to all ethylenically unsaturated material present in the composition is usually in the range of from about 0.1:100 to about 15:100; a weight ratio in the range of from about 0.1:100 to about 10:100 is preferred. From about 2:100 to about 6:100 is especially preferred.

When, as is preferred, polymerization of the polymerizable composition is initiated by thermally generated free radicals, the polymerizable composition contains initiator. The initiators which may be used in the present invention may be widely varied, but in general they are thermally decomposable to produce radical pairs. One or both members of the radical pair are available to initiate addition polymerization of ethylenically unsaturated groups in the well-known manner.

The preferred initiators are peroxy initiators. Examples of suitable peroxy initiators include those represented by any of the following formulae:



wherein  $R_{10}$  and  $R_{11}$  are each individually phenyl, phenylalkyl in which the alkyl portion is straight or branched and contains from 1 to about 10 carbon atoms, straight alkyl containing from 1 to about 20 carbon atoms, branched alkyl containing from 3 to about 20 carbon atoms, cycloalkyl containing from about 5 to about 12 carbon atoms, or polycycloalkyl containing from about 7 to about 12 carbon atoms. The specific groups used for  $R_{10}$  and  $R_{11}$  may be the same or they may be different.

It is to be understood that unless otherwise qualified, either expressly or contextually, any of the above groups may be substituted with one or more minor substituents so long as their numbers and identities do not render the initiator unsuitable for its intended purpose. Halo groups, alkoxy groups containing from 1 to about 4 carbon atoms, haloalkyl groups containing from 1 to about 4 carbon atoms, and polyhaloalkyl groups containing from 1 to about 4

carbon atoms, are examples of substituents which may be used. Alkyl groups containing from 1 to about 4 carbon atoms may be used as substituents on non-aliphatic groups or on non-aliphatic portions of complex groups.

5 The phenylalkyl groups used for  $R_{10}$ ,  $R_{11}$ , or both  $R_{10}$  and  $R_{11}$  often contain from 1 to about 4 carbon atoms in the alkyl portion. Benzyl and phenylethyl are preferred.

10 The branched alkyl groups often have at least one branch in the 1-position or the 2-position. In many cases each branched alkyl group contains from 3 to about 8 carbon atoms. Preferably, each branched alkyl group contains 3 or 5 carbon atoms.

15 Examples of branched alkyl groups that may be used include isopropyl, secondary butyl, isobutyl, tertiary butyl, 1-methylbutyl, 2-methylbutyl, tertiary pentyl, 1,2-dimethylpropyl, neopentyl, 1-methylpentyl, 2-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, and 1-ethyldecyl. Preferred are secondary butyl, tertiary butyl, and neopentyl.

20 The cycloalkyl often contains from about 5 to about 8 carbon atoms.

Examples of cycloalkyl groups include cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl, and cyclododecyl. Cyclohexyl is preferred.

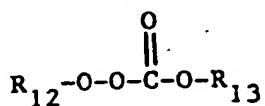
25 The polycycloalkyl typically contains from about 7 to about 10 carbon atoms.

Examples of polycycloalkyl groups that may be used include 1-norbornyl, 2-bornyl, and 1-adamantyl.

30 Exemplary peroxy initiators include those described above in respect of the preparation of liquid aromatic-containing poly(allyl carbonate) polymer. Diisopropyl peroxydicarbonate and benzoyl peroxide are the preferred initiators.

Other examples of suitable peroxy initiators include monoperoxycarbonates represented by the following formula:

35



(XIV)

wherein  $R_{12}$  is a tertiary  $C_4$ - $C_5$  alkyl, e.g., tertiary butyl and tertiary amyl, and  $R_{13}$  is a  $C_3$ - $C_7$  alkyl. Examples of alkyl radicals representative of  $R_{13}$  include: isopropyl, n-propyl, isobutyl, secondary butyl, n-butyl, secondary amyl, isoamyl, n-amyl, secondary 5 hexyl, isoheptyl, n-hexyl, n-heptyl and 2,4-dimethyl-3-pentyl.

Preferred as  $R_{13}$  are secondary  $C_3$ - $C_7$  alkyls such as isopropyl, secondary butyl, and 2,4-dimethyl-3-pentyl. Particularly preferred monoperoxy carbonates are tertiary-butylperoxy isopropyl carbonate and tertiary-amylperoxy isopropyl carbonate.

10 Only one initiator or a plurality of initiators may be used as desired.

When used, the amount of initiator present in the polymerizable, homogeneous composition may be widely varied. Ordinarily the weight ratio of the initiator to all ethylenically unsaturated 15 material present in the composition is in the range of from about 0.5:100 to about 7:100. In many cases the weight ratio is in the range of from about 1:100 to about 5:100. A weight ratio in the range of from about 2:100 to about 4:100 is preferred.

It will be recognized by those skilled in the art that the 20 most preferred weight ratios of initiator will depend upon the nature of the initiator used (its active oxygen content) as well as the nature and ratios of the variously ethylenically unsaturated materials present in the composition.

Another material which may optionally be present in the 25 polymerizable, homogeneous composition is mold release agent. When used, the mold release agent is employed in the polymerizable composition in amounts sufficient to ensure an intact, that is, unbroken and uncracked, casting which releases easily from the mold. The mold release agent should be compatible with the polymerizable 30 composition and not adversely affect the physical properties of the casting. More particularly, the mold release agent should not adversely affect the physical properties most characteristic of the polymerizable such as its rigidity, hardness, index of optical refraction, transmission of visible light and absence of coloring 35 which affects optical clarity. The mold release agent should, therefore, be a liquid or, if a solid, be soluble in the polymerizable composition.

Mold release agents that may be used include alkyl phosphates and stearates. Among the alkyl phosphates that may be used as a mold release agent are the mono and dialkyl phosphates (and mixtures of mono and dialkyl phosphates) which are commercially available from E. I. DuPont de Nemours & Co. under the trade names ORTHOLEUM® 162 and ZELEC® UN. These alkyl phosphates are reported to have straight chain alkyl groups of from 16 to 18 carbon atoms.

Other mold release agents that may be used include stearic acid and the metal salts of stearic acid, e.g., stearic acid salts of the metals zinc, calcium, lead, magnesium, barium, cadmium, aluminum, and lithium. Other fatty acids and fatty acids salts may also be used, provided that they do not adversely effect the physical properties of the casting. Other mold release agents known to the art may be used.

When used, the mold release agent is ordinarily present in the polymerizable, homogeneous composition in an amount between about 1 and about 2000 parts by weight of mold release agent per million parts by weight of all ethylenically unsaturated material present (PPM). In many cases, between about 20 and about 200 PPM is used.

Between about 25 and about 100 PPM is preferred.

Dyes are optional materials that may be present when high transmission of light is not necessary.

Further examples of optional materials that may be present include small amounts of polymerization inhibitors to promote stability during storage and ultraviolet light absorbers.

The listing of optional ingredients discussed above is by no means exhaustive. These and other ingredients may be employed in their customary amounts for their customary purposes so long as they do not seriously interfere with good polymer formulating practice.

In the polymerizable composition, the ethylenically unsaturated material should be in the form of a solution in the proportions used.

The polymerizable, homogeneous compositions of the invention are usually prepared by admixing the various ingredients. Mixing may be accompanied with heating when it is desirable to hasten dissolution of any of the ingredients. However, if initiator is present during

heating, the temperature should ordinarily be maintained below that at which polymerization is initiated. It is preferred to employ heating in the absence of initiator, to cool the resulting solution, and then to introduce the initiator and other ingredients which enter the 5 solution without undue difficulty.

The polymerizable, homogeneous compositions of the invention can be free-radically polymerized (viz., cured) by the known conventional techniques for polymerizing (allylic carbonate)-containing compositions to form solid, crosslinked 10 polymer.

Preferably, polymerization is accomplished by heating the polymerizable composition to elevated temperatures in the presence of free-radical initiator. Typically polymerization is conducted at temperatures in the range of from about 28°C to about 100°C. In many 15 cases post curing, that is, heating beyond the time thought necessary to substantially fully polymerize the composition is employed. The post cure is often carried out above about 100°C, but below the temperatures at which thermal degradation provides undesirable yellowness, e.g., about 125°C, and preferably for a time sufficient to 20 attain either substantially constant or maximum Barcol hardness. For example, when the cure cycle shown in Table 2 below is followed, the polymerizate may be maintained at 100° for an additional 1 to 4 hours or more. Although not wishing to be bound by any theory, the additional 1 to 4 hours of post cure is believed to decompose, 25 primarily by initiation and chain termination, from 83 percent to 99.9 percent of the peroxide initiator remaining unreacted at the end of the normal 18 hour cure cycle. Moreover, the additional 1 to 4 hours of cure often increases the Barcol Hardness by about 5 to 8 units.

In most cases, the polymerizable, homogeneous composition 30 is conformed to the shape of the final solid polymerized article before polymerization. For example, the composition can be poured onto a flat surface and heated, whereby to effect polymerization and form a flat sheet or coating. According to a still further exemplification, the 35 polymerizable composition is placed in molds, as for instance glass molds, and the molds heated to effect polymerization, thereby forming

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shaped articles such as lens blanks or ophthalmic lenses. In a particularly preferred embodiment, the composition is poured into a lens mold and polymerized therein to produce an ophthalmic lens.

A wide variety of cure cycles, that is, time-temperature sequences, may be used during polymerization. Ordinarily the cure cycle employed is based upon a consideration of several factors including the size of the coating, the identity of the initiator, and the reactivity of the ethylenically unsaturated material. For casting ophthalmic lenses or lens blanks, several standard cure cycles have been developed and these are shown in Tables 1-4. These standard cure cycles are useful in forming polymerizates according to the present invention, but they are, however, only exemplary, and others may be used.

0224123

Table 1

Standard Cure Cycle for Diisopropyl Peroxydicarbonate

	<u>Cumulative Hours</u>	<u>Oven Temperature, °C</u>
5	0	44
	2	46
	4	48
	6	50
	8	54
	10	58
10	12	64
	14	69
	16	85
	17	105 (End of Cycle.)

Table 2

Standard Eighteen Hour Cure Cycle for Benzoyl Peroxide

	<u>Cumulative Hours</u>	<u>Oven Temperature, °C</u>
20	0	63
	2	63
	4	65
	6	67
	8	77
	10	80
25	12	85
	14	88
	16	92
	18	100 (End of Cycle.)

Table 3

Standard Five Hour Cure Cycle for Benzoyl Peroxide

	<u>Cumulative Hours</u>	<u>Oven Temperature, °C</u>
30	0	90
	1	90
	2	90
	3	90
	3.5	96
	4	103
35	4.5	109
	5	115 (End of Cycle.)

Table 4

Standard Cure Cycle for Tertiary-Butylperoxy Isopropyl Carbonate

	<u>Cumulative Hours</u>	<u>Oven Temperature, °C</u>
5	0	90
	2	91
	4	92
	6	93
	8	95
	10	97
10	12	100
	14	103
	16	110
	17	120 (End of Cycle.)

The polymerizates of the present invention, on an undyed and 15 untinted basis, not only have high refractive indices, but they also exhibit low yellowness and 15-second Barcol hardness values which are acceptable for ophthalmic purposes. Prior to the present invention, the achievement of all three properties concurrently in a polymerizate was accomplished only with difficulty.

20 The present polymerizates have 15-second Barcol hardnesses of at least zero. In many cases the Barcol hardness is at least about 15, and preferably it is at least about 25. As used herein, 15-second Barcol hardness is determined in accordance with ASTM Test Method D 2583-81 using a Barcol Impressor and taking scale readings 15 seconds 25 after the impressor point has penetrated the specimen.

The present polymerizates on an undyed and untinted basis, also have yellowness indices at a sample thickness of about 3.3 millimeters of about 4 or lower. Often the yellowness index is about 2.5 or lower. Preferably, the yellowness index is about 1.5 or 30 lower. As used herein, yellowness index is determined on specimens having a thickness of about 3.3 millimeters in accordance with ASTM Test Method D 1925-70 (Reapproved 1977) using a Hunterlab Tristimulus Colorimeter Model D25P employing a collimated Illuminant C standard light source.

35 The present polymerizates also have refractive indices at 20°C and a wavelength of 589.3 nanometers of at least about 1.52.

Often the refractive index under the same conditions is at least about 1.53. Preferably it is at least about 1.55.

In many cases the polymerizates of the present invention, on an undyed and untinted basis, also exhibit one or more other favorable 5 properties. Among these favorable properties may be mentioned high luminous transmission, low haze, a density of about 1.3 grams per cubic centimeter or lower and low heat distortion.

As used herein luminous transmission and haze value are determined on specimens having a thickness of about 3.3 millimeters in 10 accordance with ASTM Test Method D 1003-61 (Reapproved 1977) using a Hunterlab Tristimulus Colorimeter Model D25P employing a collimated Illuminant C standard light source. As the luminous transmission approaches one hundred percent, the difference in luminous transmissions for two samples of the same material but of differing 15 thicknesses approaches zero. Consequently, values of luminous transmission of about 90 percent or greater ascertained from samples having thicknesses within about a millimeter of the 3.3 millimeter standard, approximate reasonably well the luminous transmission at the standard thickness. In similar fashion, haze values of about one 20 percent or less ascertained on samples having thicknesses within about a millimeter of the 3.3 millimeter standard, approximate reasonably well the haze value at the standard thickness. Although the yellowness index seems to vary more with sample thickness than luminous transmission or haze value, nevertheless yellowness indices 25 ascertained from samples having thicknesses within about a millimeter of the 3.3 millimeter standard do provide a useful general indication of the yellowness index at the standard thickness.

In most cases the luminous transmission of the present polymerizates on an undyed and untinted basis, is at least about 80 30 percent. Frequently the luminous transmission is at least about 85 percent. Preferably the luminous transmission is at least about 90 percent. When the polymerizate is dyed or tinted for use in sunglasses or filters, the luminous transmission of the dyed and/or tinted, sample is usually at least about 20 percent.

35 Often the haze value of the polymerizates, on an undyed and untinted basis is about 5 percent or lower. In many cases the haze

value is about 4 percent or lower, and preferably it is about 2 percent or lower.

The density of most of the polymerizates of the invention is usually about 1.3 grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ) or lower.

5 Frequently the density is about  $1.27 \text{ g}/\text{cm}^3$  or lower, and preferably it is about  $1.25 \text{ g}/\text{cm}^3$  or lower. As used herein, density is determined in accordance with ASTM Test Method C729-75 and reported for a temperature of  $25^\circ\text{C}$ .

The heat distortion test is conducted as described in ASTM 10 Standard Test Method D 648-72. Preferably the heat distortion temperature of the polymerizates of the present invention is at least  $45^\circ\text{C}$ .

The invention is further described in conjunction with the following examples which are to be considered illustrative rather than 15 limiting, and in which all parts are parts by weight and all percentages are percentages by weight unless otherwise specified.

#### EXAMPLE I

A casting solution was formed by admixing 100 parts of bisphenol A bis(allyl carbonate) monomer and 1.8 parts of diisopropyl 20 peroxydicarbonate.

A portion of the casting solution was charged into a glass mold constructed of two glass sheets separated by a pliable gasket that was about 3.56 millimeters thick. The glass mold was held together by large binder clips. After filling the mold, it was placed 25 in a hot air oven and exposed to the Standard Cure Cycle for Diisopropyl Peroxydicarbonate of Table 1. When the cure cycle was completed, the mold was removed from the oven and allowed to cool to room temperature. The resulting polymerizate was then removed from the mold and was found to be about 3.4 millimeters thick. Various 30 properties of the polymerizate are shown in Table 5.

Table 5

Yellowness Index (3.4 mm thickness)	4.8
35 Barcol Hardness	
0-second	39
15-second	39

EXAMPLE II

A casting solution was formed by admixing 99 parts of bisphenol A bis(allyl carbonate) monomer, one part of  $\alpha$ -terpinyl acetate, and 1.8 parts of diisopropyl peroxydicarbonate. A sheet of 5 polymerizate was prepared from the casting solution according to the procedure of Example I. The polymerizate was found to be about 3.3 millimeters thick. Various properties of the polymerizate are shown in Table 6.

Table 6

10	Yellowness Index (3.3 mm thickness)	2.0
	Barcol Hardness	
15	0-second	36
	15-second	36

EXAMPLE III

A casting solution was formed by admixing 294 parts of bisphenol A bis(allyl carbonate) 6 parts of  $\alpha$ -terpinyl acetate, and 20 5.4 parts of diisopropyl peroxydicarbonate. A sheet of polymerizate was prepared from the casting solution according to the procedure of Example I. The polymerizate was found to be about 3.3 millimeters thick. Various properties of the polymerizate are shown in Table 7.

Table 7

25	Yellowness Index (3.3 mm thickness)	1.2
	Luminous Transmission, percent (3.3 mm thickness)	92.8
30	Haze Value, percent (3.3 mm thickness)	0.3
	Barcol Hardness	
35	0-second	35
	15-seconds	34
	Refractive Index, $n_D^{20}$	1.5626, 1.5617, 1.5620
40	Abbe Number	37.7
	Heat Distortion Temperature (264 psi; 1820 kPa), $^{\circ}$ C	54, 50

EXAMPLE IV

A casting solution was formed by admixing 39.6 parts of bisphenol A bis(allyl carbonate) monomer, 0.4 parts of cyclohexene, and 0.8 part of diisopropyl peroxydicarbonate. A sheet of 5 polymerizate was prepared from the casting solution according to the procedure of Example I. The polymerizate was about 3.3 millimeters thick. Various properties of the polymerizate are shown in Table 8.

Table 8

10	Yellowness Index (3.3 mm thickness)	1.2
15	Luminous Transmission, percent (3.3 mm thickness)	91.9
20	Haze Value, percent (3.3 mm thickness)	0.6
	Barcol Hardness 0-second	21
	15-seconds	16

EXAMPLE V

A first solution was formed by admixing 472.5 parts of bisphenol A bis(allyl carbonate) monomer, 7.5 parts of  $\alpha$ -terpinyl 25 acetate, 5.0 parts of benzyl acetate, 2.5 parts of cyclohexene, 2.5 parts of cyclohexanone, and 10 parts of diethylene glycol bis(allyl carbonate) monomer.

A casting solution was formed by admixing 100 parts of the above first solution, 3 parts of diisopropyl peroxydicarbonate, and 30 0.005 part of Zelec<sup>®</sup> UN mold release agent.

A sheet of polymerizate was prepared from the casting solution according to the procedure of Example I. The polymerizate was found to be about 3.2 millimeters thick. Various properties of the polymerizate are shown in Table 9.

Table 9

Yellowness Index (3.2 mm thickness)	1.1
5 Luminous Transmission, percent (3.2 mm thickness)	92.1
Haze Value, percent (3.2 mm thickness)	0.5
10 Barcol Hardness	
0-second	39
15-seconds	37
15 Heat Distortion Temperature (264 psi; 1820 kPa), °C	67.5

EXAMPLE VI

A first solution was formed by admixing 922.5 parts of 20 bisphenol A bis(allyl carbonate) monomer, 13.6 parts of  $\alpha$ -terpinyl acetate, 9 parts of benzyl acetate, 4.5 parts of cyclohexene, 4.5 parts of cyclohexanone, and 45.5 parts of isobutyl methacrylate.

A casting solution was formed by admixing 100 parts of the above first solution, 3 parts of diisopropyl peroxydicarbonate, and 25 0.005 part of Zelec® UN mold release agent. A sheet of polymerizate was prepared from the casting solution according to the procedure of Example I except that the pliable gasket was about 2.84 millimeters thick. The polymerizate was found to be about 2.76 millimeters thick. Various properties of the polymerizate are shown in Table 30 10.

Table 10

Yellowness Index (2.76 mm thickness)	1.0
35 Barcol Hardness	
0-second	32
15-seconds	30
40 Refractive Index, $n_D^{20}$	1.5554

EXAMPLE VII

A first solution was formed by admixing 940 parts of bisphenol A bis(allyl carbonate) monomer, 15 parts of  $\alpha$ -terpinyl acetate, 15 parts of benzyl acetate, and 30 parts of diethylene glycol bis(allyl carbonate) monomer.

A casting solution was formed by admixing 100 parts of the above first solution, 2 parts of diisopropyl peroxydicarbonate, and about 0.005 part of Zelec® UN mold release agent. A sheet of polymerizate was prepared from the casting solution according to the 5 procedure of Example I. The polymerizate was found to be about 3.4 millimeters thick. Various properties of the polymerizate are shown in Table 11.

Table 11

10	Yellowness Index (3.4 mm thickness)	1.2
	Luminous Transmission, percent (3.4 mm thickness)	92.0
15	Haze Value, percent (3.4 mm thickness)	0.6
20	Barcol Hardness 0-second	43
	15 seconds	42
	Refractive Index, $n_D^{20}$	1.5597, 1.5599
25	Abbe Number	37.7
	Heat Distortion Temperature (264 psi; 1820 kPa), °C	64, 64
30	Density at 25°C, g/cm <sup>3</sup>	1.224

EXAMPLE VIII

A first solution was formed by admixing 2835 parts of bisphenol A bis(allyl carbonate) monomer, 45 parts of  $\alpha$ -terpinyl acetate, 30 parts of benzyl acetate, 15 parts of cyclohexene, 15 parts 35 of cyclohexanone, and 60 parts of diethylene glycol bis(allyl carbonate) monomer.

A second solution was formed by admixing 1000 parts of the above first solution, 40 parts of isobutyl methacrylate, and 12.5 parts of 4-bromodiphenyl.

40 A casting solution was formed by admixing 100 parts of the above second solution and 3 parts of diisopropyl peroxydicarbonate. A sheet of polymerizate was prepared from the casting solution according to the procedure of Example I except that the pliable gasket was about

2.84 millimeters thick. The polymerizate was found to be about 2.51 millimeters thick. Various properties of the polymerizate are shown in Table 12.

Table 12

5	Yellowness Index (2.51 mm thickness)	1.2
10	Barcol Hardness 0-second	37
	15-second	35
20	Refractive Index, $n_D^{20}$	1.5582

EXAMPLE IX

15 A stock solution was formed by admixing 451.6 parts of  $\alpha$ -terpinyl acetate, 290.3 parts of benzyl acetate, 112.9 parts of cyclohexene, and 145.2 parts of cyclohexanone.

A first solution was formed by admixing 12.4 parts of the above stock solution, 10 parts of vinyl acetate, and 377.6 parts of 20 bisphenol A bis(allyl carbonate) monomer.

A first casting solution was formed by admixing 100 parts of the above first solution and 3 parts of diisopropyl peroxydicarbonate.

25 A second solution was formed by admixing 12.4 parts of the above stock solution, 14 parts of vinyl acetate, and 373.6 parts of bisphenol A bis(allyl carbonate) monomer.

A second casting solution was formed by admixing 100 parts of the above second solution and 3 parts of diisopropyl peroxydicarbonate.

30 A third solution was formed by admixing 12.4 parts of the above stock solution, 20 parts of vinyl acetate, and 367.6 parts of bisphenol A bis(allyl carbonate) monomer.

A third casting solution was formed by admixing 100 parts of the above third solution and 3 parts of diisopropyl 35 peroxydicarbonate.

Sheets of first, second, and third polymerizates were prepared respectively from the first, second, and third casting solutions according to the procedure of Example I except that the pliable gasket for each mold was about 2.84 millimeters thick. The 40 thicknesses of the first, second, and third polymerizates were found

to be about 2.49, 2.45, and 2.57 millimeters, respectively. Various properties of the polymerizates are shown in Table 13.

Table 13

		Polymerizate		
		<u>First</u>	<u>Second</u>	<u>Third</u>
5	Yellowness Index			
	(2.49 mm thickness)	1.2		
	(2.45 mm thickness)		1.3	
	(2.57 mm thickness)			1.4
10	Luminous Transmission, percent			
	(2.49 mm thickness)	92.0		
	(2.45 mm thickness)		92.3	
	(2.57 mm thickness)			92.4
15	Haze Value, percent			
	(2.49 mm thickness)	0.3		
	(2.45 mm thickness)		0.4	
	(2.57 mm thickness)			0.5
20	Barcol Hardness			
	0-second	34	37	38
	15-seconds	33	37	37
25	Refractive Index, $n_D^{20}$	1.5592	1.5573	1.5554
		1.5594	1.5575	1.5560
				1.5558

EXAMPLE X

30 A first solution was formed by admixing 15 parts of  $\alpha$ -terpinyl acetate, 5 parts cyclohexene, 50 parts of vinyl acetate, and 930 parts of bisphenol A bis(allyl carbonate) monomer.

A casting solution was formed by admixing 100 parts of the above first solution and 2.75 parts of diisopropyl peroxydicarbonate.

35 A sheet of polymerizate was prepared from the casting solution according to the procedure of Example I except that the pliable gasket was about 2.84 millimeters thick. The polymerizate was found to be about 2.44 millimeters thick. Various properties of the polymerizate are shown in Table 14.

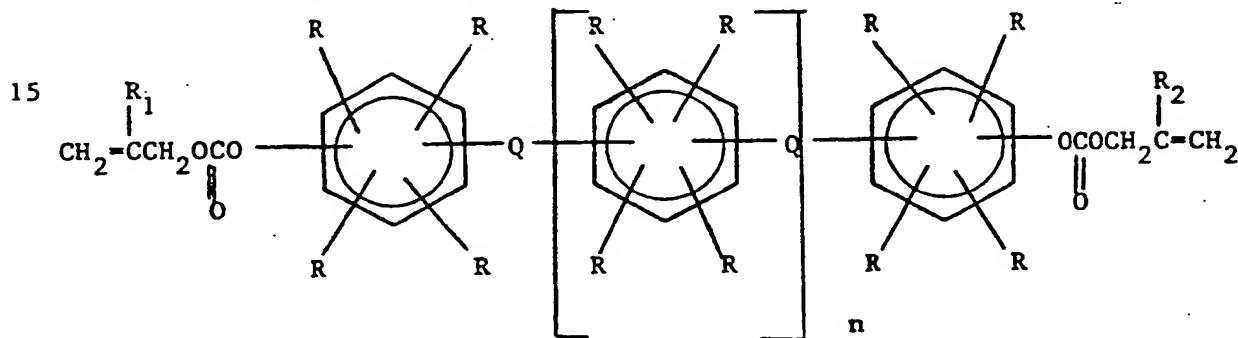
Table 14

Yellowness Index (2.44 mm thickness)	1.1
5 Luminous Transmission, percent (2.44 mm thickness)	92.7
Haze Value, percent (2.44 mm thickness)	0.6
10 Barcol Hardness	
0-second	36
15 seconds	35
15 Refractive Index, $n_D^{20}$	1.5564, 1.5563
Abbe Number	37.7
20 Density at 25°C, g/cm <sup>3</sup>	1.217
25	Although the present invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details should be regarded as limitations upon the scope of the invention except insofar as they are included in the accompanying claims.

CLAIMS:

1. A polymerizable, homogeneous composition comprising bisphenol bis(allylic carbonate)-functional material comprising (i) bisphenol bis(allylic carbonate)-functional monomer, (ii) prepolymer 5 of said monomer, or (iii) a mixture thereof, characterized in that said composition also comprises a yellowness reducing amount of (a) cyclohexenic material which is a cyclohexenic compound or a mixture of such cyclohexenic compounds, and optionally (b) one or more other materials.

10 2. The polymerizable, homogeneous composition of Claim 1 characterized in that said bisphenol bis(allylic carbonate)-functional material comprises a bisphenol bis(allylic carbonate)-functional monomer represented by the formula



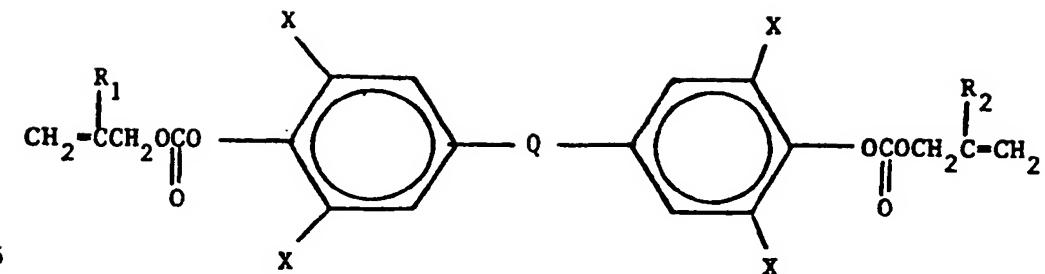
(a) each R of said monomeric compound is independently hydrogen, halo, alkyl, or alkoxy;

(b) each Q of said monomeric compound is independently oxy, sulfonyl, thio, alkanediyl, or alkylidene;

25 (c)  $R_1$  and  $R_2$  are each independently hydrogen or methyl; and

(d) the value of  $n$  is an integer in the range of from 0 to about 3.

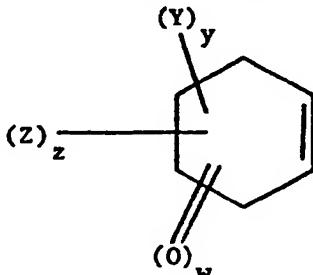
3. The polymerizable, homogeneous composition of Claim 1 characterized in that said bisphenol bis(allylic carbonate)-functional material comprises a bisphenol bis(allylic carbonate)-functional monomer represented by the formula



- (a) each X of said monomeric compound is independently hydrogen, chloro, or bromo;
- (b) Q is oxy, sulfonyl, thio, alkanediyl, or alkylidene; and
- (c) R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or methyl.

10 4. The polymerizable, homogeneous composition of Claim 3 characterized in that each X is hydrogen, Q is 1-methylethylidene, and 15 R<sub>1</sub> and R<sub>2</sub> are both hydrogen.

20 5. The polymerizable, homogeneous composition of Claim 1 characterized in that said cyclohexenic material comprises at least one cyclohexenic compound represented by the formula:



in which

25

- (a) each Y is independently alkyl containing from 1 to about 4 carbon atoms;
- (b) Z is hydroxyl, 2-oxoethyl, alkoxy carbonyl containing from 2 to about 5 carbon atoms, or R<sub>3</sub>C(O)OR<sub>4</sub><sup>-</sup> in which R<sub>3</sub> is alkyl containing from 1 to about 4 carbon atoms and R<sub>4</sub> is alkanediyl containing from 2 to about 4 carbon atoms or alkylidene containing from 1 to about 5 carbon atoms;
- (c) y is an integer in the range of from 0 to about 3;
- (d) z is 0 or 1;

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- (e) w is 0 or 1; and
- (f) the sum of z and w is 0 or 1.

6. The polymerizable, homogeneous composition of Claim 1 characterized in that said cyclohexenic material comprises at least 5 one cyclohexenic compound selected from the group consisting of cyclohexene,  $\alpha$ -terpinyl acetate,  $\alpha$ -terpinyl propionate, and  $\alpha$ -terpinyl butyrate.

7. The polymerizable, homogeneous composition of Claim 1 characterized in that said cyclohexenic material is cyclohexene, 10  $\alpha$ -terpinyl acetate, or a mixture thereof.

8. The polymerizable, homogeneous composition of any of the preceding claims characterized in that said composition comprises at least one vinyl ester of a saturated monocarboxylic acid.

9. The polymerizable, homogeneous compositions of Claim 8 15 characterized in that said vinyl ester is vinyl acetate.

10. The polymerizable, homogeneous composition of any of the preceding claims characterized in that said composition comprises peroxy initiator.

11. A polymerizate characterized in that said polymerizate 20 is produced by free-radically polymerizing the pourable, homogeneous composition of any of the preceding claims, and said polymerizate has a 15-second Barcol hardness of at least zero, a yellowness index at a sample thickness of about 3.3 millimeters of about 4 or lower, and a refractive index at 20°C and a wavelength of 589.3 nanometers of at 25 least about 1.52.

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## EUROPEAN PATENT APPLICATION

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㉔ Compositions for producing polymers of high refractive index and low yellowness.

㉕ The yellowness of polymerizates formed from polymerizable compositions containing bisphenol bis(allylic carbonate)-functional material is reduced by inclusion of one or more cyclohexenic compounds in the polymerizable compositions.

EP 0 224 123 A3



European Patent  
Office

EUROPEAN SEARCH REPORT

0224123

Application Number

EP 86 11 5687

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)		
A	EP-A-0 144 782 (PPG INDUSTRIES, INC.) * Claims 1,2; page 13, line 1 - page 14, line 3 * --- A FR-A-2 542 002 (SODAP) * Claims * -----	1	C 08 F 218/24 G 02 B 1/04		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)		
			C 08 F C 08 K G 02 B		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	16-11-1988	DE ROECK R.G.			
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A : technological background	D : document cited in the application				
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